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## (54) CATALYST SUPPORT AND PROCESS FOR ITS MANUFACTURE

(71) We, FELDMUHL ANLAGEN-UND PRODUKTIONSGESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG, a body corporate organized according to the laws of Germany, of Düsseldorf-Oberkassel, Fritz-Vomfelde-Platz No. 4, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a catalyst support of sintered inorganic material for the detoxication of exhaust gases, and a process for its manufacture.

Catalysts of sintered inorganic material are being used to an increasing extent wherever high temperature conditions arise and aggressive media come into contact with the materials, and high temperature resistance, resistance to thermal shock and corrosion resistance are important factors. These demands are made to a very particular extent of catalyst supports in chemical processes and especially in the detoxication of exhaust gases, especially the exhaust gases of motor vehicles.

Since high activity coupled with minimum possible space requirement is important in the last-mentioned processes, the exhaust gas catalyst has been given a shape which is largely determined by the end use, in that it possesses a large number of continuous channels or is given a honeycomb structure through ribbing.

These catalyst supports have also proved entirely satisfactory for stationary installations but have the disadvantage, especially for the end use of exhaust gas de-

toxication which in the present case is of particular interest, that they do not withstand the mechanical stresses which arise at the same time, for example, those which occur as a result of the constant vibrations when driving motor vehicles. It is either necessary to make the walls of the catalyst support relatively thick or to tolerate their working life being relatively short as a result of wear, crumbling or even breakage. German Offenlegungsschrift No. 1,476,505 proposes to remedy this by making the walls of the housing re-adjustable to follow the catalyst support, and furthermore providing elastic intermediate members. As a result it is admittedly more easily possible to absorb impacts and the like, but additional constructional measures are required, which furthermore have the disadvantage that the devices required for the purpose, which are metal, are attacked by the hot corrosive gases.

A further disadvantage of the previously known catalyst supports is that their manufacture is relatively expensive. The starting material for these catalyst supports consists of inorganic powders, for example aluminium oxide, which are extruded, together with a plasticiser, in tape form and are then ribbed by means of ribbing rollers. The shaping of very thin sheets of inorganic powders mixed with plasticisers, which in the uncalcined state have only low strength, is only possible by special methods. Thus, for example, a process described in German Patent Specification No. 1,097,344 consists of applying the ceramic raw material together with the binder to a support, for example a paper web or foil web, with this support material providing 80

the requisite strength and dimensional stability for subsequent processing, such as ribbing by means of toothed wheels. These support materials are then removed on cal-

5 cining the ceramic body. Here it is however a distinct disadvantage that these organic support materials are already burnt off at substantially lower temperatures than are required for sintering, so that the

10 shaped articles in question are without this supporting protection at the actual sintering temperature, at which they receive their strength and their rigid lattice. A further disadvantage of the previously known cata-

15 lyst supports is that their mechanical strength is not sufficiently great for the above-mentioned end use, especially if the wall thickness of these catalyst supports is kept very low.

20 The shaping of very thin "green" ceramic materials always presents a particularly difficult problem. Hence, in the process previously described a support is coated and subsequently shaped. However, even with

25 ceramics supported in this way the shaping must still be carried out very carefully and very slowly. This inadequate speed of manufacture is one of the serious disadvantages of this process.

30 The present invention provides a manufacturing process for a catalyst support which is relatively inexpensive so a mass-produced product can be relatively cheap to manufacture. It also provides catalyst

35 supports which have a large active surface and sufficient strength to stand severe thermal and mechanical stresses encountered in motor vehicles, and so that their working

40 life corresponds as far as possible to that of the motor vehicle.

The present invention provides a process for the manufacture of a catalyst support consisting of layers of refractory inorganic material, at least every alternate layer

45 being corrugated, wherein a fleece blank consisting of layers of fibrous fleece material comprising refractory inorganic fibres, at least every alternate layer being

50 corrugated, is covered with a slip of refractory inorganic material, dried and sintered at a temperature within the range of from 1200 to 1800°C, the refractory inorganic material of the slip and the refractory inorganic fibres of the fleece blank

55 being so selected that on sintering the slip material and the fibrous material are sintered together.

The fleece blank may be prepared by corrugating a first fleece, applying it to a

60 second fleece, which may or may not be corrugated, and shaping the resulting assembly, or arranging and/or shaping a plurality of such assemblies, to form a desired structure in which at least every al-

65 ternate fleece layer is corrugated. Prefer-

ably the second fleece is substantially flat, so that the resulting fleece blank has alternate corrugated and substantially flat layers.

The shaping may, for example, consist 70 of rolling up a two-fleece assembly as described above to give a fleece blank having a circular or oval cross-section; alternatively, a plurality of such two-fleece assemblies may be stacked to give an article 75 having a square or rectangular cross-section.

The individual layers of the fleece blank may be bonded together with, for example, water-glass.

As a result of the processes according to 80 the invention, the difficulties of shaping ceramic material can be avoided by using the techniques of paper manufacture and processing paper into corrugated cardboard 85 with its associated speed. This coupled with the advantage that the actual shaping of the catalyst support, that is to say, corrugation followed by, for example, rolling 90 up to give structures of for example circular, oval or square cross-section, is carried out solely with the support fleece and that the fleece blank which already largely has its shape is then impregnated with the slip of refractory inorganic material, so 95 that the refractory inorganic materials do not themselves have to be subjected to any actual shaping. In this way the plasticisers and equipment, such as extruders, and the associated process stages otherwise needed, 100 can be avoided.

The inorganic fibres of the fleece blank impart strength to the shaped article during sintering until the sintering process has progressed to the point that the slip has sufficient strength in itself. This dimensional stability should be provided, in the case of slips rich in  $Al_2O_3$ , up to temperatures of 1000° to 1200°C.

As high temperature-resistant inorganic 110 fibres for the fibrous fleece material there are preferably used fibres which possess a certain material similarity to the refractory inorganic materials in the slip. When using compositions rich in aluminium oxide in 115 the slip, a fleece of fibres with a considerable proportion of aluminium oxide, for example mullite or sillimanite, is preferably used.

A fleece of kaolin wool, which is distinguished by good ease of sintering and stability, has proved particularly successful. These aluminosilicate fibres have a low specific gravity of 2.56 g/cm<sup>3</sup> and are flexible and elastic; their aluminium oxide 125 content is 43 to 47% and their silicon oxide content is 50 to 54%. In the manufacture of the fleece, the fibres which are up to 250 mm long are comminuted to a length of approximately 4 mm. 130

Because of the relationship between refractory inorganic fibres and refractory inorganic materials which are high temperature-resistant and temperature variation-resistant, the support fleece sinters to the inorganic materials and thus a strong and intimate bond is achieved without subsequently impairing the good mechanical and thermal properties of the inorganic materials of the slip because of excessive difference between the materials.

It has proved particularly successful to manufacture the support fleece of a mixture of refractory inorganic fibres and organic fibres. The organic fibres have three functions; they facilitate fleece formation, they improve the ease of shaping, and their presence results in the production of pores and channels in the finished catalyst support.

The organic fibres may be either natural or synthetic; combinations of natural and synthetic fibres can also be used. When using exclusively artificial organic fibres, those which can be split into fibrils are particularly suitable since thereby adhesion to the inorganic fibres is ensured.

The shaping of the fibrous fleece material may appropriately be carried out on a so-called corrugated board machine known from the paper industry, on which structures consisting of flat and corrugated layers can be manufactured at high speed. These shaping devices achieve working speeds of approximately 100 m/minute for the production of, for example, a corrugation having a half wave-height of 1.8 mm and a half wave-length of 4.0 mm. (The terms "half wave-height" and "half wave-length" are explained below with reference to Figure 1 of the accompanying drawings.) Standard ribbing devices, in contrast, work at substantially lower speeds of at most 10 mm/minute.

Following the corrugation, a corrugated fleece layer and a flat fleece layer may be brought together so that a corrugated board structure is produced by the alternately superposed corrugated and flat layers. This results in better maintenance of the spacing since otherwise the corrugated sheets would fit into one another.

Especially for use in a restricted space it is advantageous to roll up or stack the support fleece, before covering with slip, to give a fleece blank of, for example, circular, oval or square cross-section or to give a spiral.

The slip of refractory material can be applied in various ways to the fleece blank. Impregnation has proved successful as a problem-free and rapid process. The impregnation can be carried out by immersing the fleece blank in the slip or by pouring the slip over the fleece blank.

In an advantageous embodiment, the support fleece consists of 20 to 90%, preferably 20 to 50%, of refractory inorganic fibres and 80 to 10%, preferably 80 to 50%, of organic fibres. These organic fibres can appropriately be exclusively or partly cellulose fibres. They have the advantage that because of their fibrillar structure they facilitate fleece formation and the corrugation and shaping of the fleece. When conjointly using other organic fibres the proportion of cellulose fibres is advantageously at least 5%, based on the total weight of fibres in the support fleece material, in order to ensure good fleece formation and deformability. All data on proportions of fibres relate to per cent by weight. The conjoint use of organic fibres facilitates to a very considerable extent the formation of a fleece from refractory inorganic fibres.

The conjoint use of organic fibres has the additional advantage that the porosity of the finished catalyst support can be controlled through the fibres which are burnt away during sintering. This is particularly important for the absorption of catalyst material to be applied subsequently to the support by impregnation, and because it results in a substantially greater geometrical surface area for the detoxication of the exhaust gases. This macroscopic porosity, which is so important, is determined to a substantial degree by the organic fibres which are burnt away and can therefore be controlled through the proportion of organic fibres.

It has been found that the impregnation with slip is greatly facilitated by an open fleece of relatively low-density packing. This low-density packing in the fleece material is already achieved to a considerable degree by the proportion of rigid refractory inorganic fibres and can be further increased through the choice and diameter of the organic fibres, for example by the use of non-ground cellulose.

The support fleece used for the manufacture of the catalyst support is advantageously 0.1 to 0.5 mm, preferably 0.15 to 0.3 mm, thick and preferably has a weight per unit area of 25 to 60 g/m<sup>2</sup> in order to achieve a satisfactorily low weight and a large active surface area in the catalyst support.

A two-stage impregnation wherein the catalyst support, after sintering, is again covered with slip and is sintered at lower temperatures, appropriately 1200° to 1400°C, is particularly advantageous. The second sintering process, taking place at lower temperatures, results in a substantially higher specific surface area. The essential strength is achieved by the first calcination, in which the slip sinters rela-

tively densely. During the second calcination, at lower temperatures, the slip is not sintered so densely and instead remains porous and thus produces additional active surface.

The refractory inorganic materials used for the slip, withstand high temperatures and temperature variation well and have high mechanical strength. They are especially the high-melting oxides, nitrides, carbides, borides, and silicides which are in themselves known and which are characterised by high mechanical strength, temperature resistance, chemical resistance and abrasion resistance. Silicon nitride also withstands temperature variation particularly well.

Compositions containing aluminium oxide have proved particularly successful because they can be manufactured economically and because of their thermal and mechanical properties. Such compositions are used in a finely powdered form, for example, with a specific surface area of  $3 \text{ m}^2/\text{g}$ .

The slip preferably comprises an aqueous suspension of aluminium oxide powder. Depending on the density of the stacked or wound-up support fleece, the slip contains 20 to 90% of solids, a content of between 40 and 70% being preferred.

In the preferred end use, the catalyst supports manufactured according to the invention serve for the detoxication of industrial exhaust gases or motor vehicle exhaust gases. Possible catalytic substances are the customary inorganic catalysts such as oxides, cerates, chromates, chromites, manganates, manganites and vanadates of metals such as iron, cobalt, nickel, palladium, platinum, ruthenium, rhodium, manganese, chromium, copper molybdenum, tungsten and the rare earth metals. The noble metals such as ruthenium, rhodium, platinum and palladium can also be used in the free form.

The catalysts can be applied to the catalyst support by known processes. Thus, the catalyst support can be subsequently sprayed or impregnated with the catalytically active substance, or the latter can be incorporated into the catalyst support in some other manner. A known method is the application of a soluble salt of the catalytically active metal, which is converted *via* precipitation, deposition, drying and calcination into the catalytically active oxide, chromite or the like.

The process according to the invention of impregnating a preformed fleece blank with slip offers the further advantage that the composition of this slip can be varied much more extensively than is possible in the case of compositions which are to be

extruded. For example, the slip itself may advantageously contain catalytically active substances. It is even possible for the refractory inorganic material in the slip to be itself catalytically active, for example to consist of cerium oxide.

These two embodiments have the advantage that even if there is a certain amount of abrasion in use which can never be entirely avoided, as a result of the exhaust gases flowing past the material, new catalytically active surfaces are constantly exposed.

The invention also provides a catalyst support manufactured according to the process of the invention, which presents substantial advantages over the previously known catalyst supports. The catalyst support meets the essential requirements of high temperature resistance, resistance to thermal shock, mechanical stability to impact, vibration and erosion, corrosion resistance and resistance to oxidation. The support fleece of inorganic fibres largely eliminates the brittleness which is, in particular, inherent in sintered articles of compositions rich in aluminium oxide.

It has been found that the support fleece of refractory inorganic fibres is sintered into the refractory inorganic material of the slip. When using inorganic fibres containing silicate, such as, for example, kaolin, regions enriched in  $\text{SiO}_2$  are produced within the layers.

In this way, a catalyst support preferably consisting of corrugated and flat layers which are alternately superposed and which have the shape required for fitting, may be produced. These layers consist of refractory inorganic fibres sintered together with slip.

When organic fibres are conjointly used in the manufacturing process for inherently entirely different reasons, namely, for facilitating initial formation of the fleece and improving the ease of shaping thereof, the resulting catalyst support possesses additional internal pores in the positions where the organic fibres, preferably cellulose fibres, of the support fleece were present.

A catalyst support according to the invention having the preferred arrangement of alternating corrugated and flat layers has the particularly advantageous characteristic that the overall layer thickness at the bonds between the flat and corrugated layers is not substantially greater than that of the individual layers. The bonds of the flat and corrugated layers as a result have particularly high strength. This high strength is probably associated with the fact that at the points of contact a corrugated and a smooth layer of the support fleece are directly sintered to one another

to form a flexible support. At these points of contact there appears for the sintering of the slip of the corrugated layer with the slip of the smooth layer a particularly large reaction area. In contrast to this, when joining together a corrugated and a smooth layer which consists exclusively of ceramic slip, only a point-like bonding can be achieved. In addition, this arrangement contributes considerably to the manufacture of a thin-walled catalyst support.

It has been found that in the case of radially acting clamping devices the compressive breaking resistance of the ceramic catalyst support can be exceeded locally. A fixing, for example, by screws can easily become the starting point for the mechanical destruction of the catalyst support. In addition, the brittleness which is inherent in ceramic sintered articles represents a considerable difficulty for the end use of exhaust gas detoxication which is here of prime importance. This is because there is the danger that support bodies may not be able to withstand the mechanical stresses which arise, for example, as a result of the constant vibrations when driving motor vehicles.

According to a further advantageous embodiment of the invention, these difficulties are solved through the catalyst support being surrounded by a mechanically strong refractory outer jacket of shrinkage-free ceramic cement (as hereinafter defined).

Ceramic cements contain a high proportion of aluminium oxide constituents. As a result of the similarity in material of the cement jacket and a catalyst support of high aluminium oxide content, a composite results which remains stable even at high temperatures and under frequent temperature variation, such as results from starting and switching off of the motor.

The essential advantage of the outer jacket of ceramic cement lies in the extraordinary increase in the radial compressive breaking resistance. Catalyst supports without an outer jacket have a radial compressive breaking resistance of 3 to 7 kg/cm<sup>2</sup>. A 1 mm thick outer jacket of ceramic cement causes an increase in the compressive breaking resistance to over 100 kg/cm<sup>2</sup>.

Customary ceramic cements undergo a shrinkage of 0.25 to 0.30 % during consolidation whilst the catalyst support expands during a thermal consolidation. As a result, cracks can arise in the cement jacket, which propagate in the support body and cause mechanical destruction.

The surprising solution of this technical problem consists of a ceramic cement which consolidates without crack formation. By shrinkage-free cement there is here understood a cement in which the chemical

shrinkage is compensated by flaws, such as, for example, micro-cracks or pores. The surprising technical effect which is achieved by the use of a shrinkage-free ceramic cement is probably based on the fact that the stress cracks which result during consolidation expend themselves in a large number of small pores. This prevents the cracks from building up into a small number of large cracks and instead they remain dispersed in a large number of small cracks in the outer jacket, whereby the strength of the outer jacket is not significantly reduced and propagation into the catalyst support is prevented.

An outer jacket of an aluminium phosphate-bonded cement has proved particularly appropriate. Apart from the phosphoric acid required for setting, and optionally other additives, this ceramic cement consists exclusively of aluminium oxide. In this way a particularly intimate bond between the outer jacket and the catalyst support is achieved with ceramic catalyst supports having a high aluminium oxide content and a sintered-in ceramic fibre fleece.

A further aspect of the invention comprises a process for the manufacture of the catalyst support with an outer jacket, referred to above, which consists of covering the catalyst support, after sintering, with a slurry of shrinkage-free ceramic cement and allowing the cement to dry and set at a temperature of 200 to 1,000°C.

The particular advantage of the use of a ceramic cement lies in the low drying and setting temperatures of 200° to 1,000°C, preferably 200° to 500°C.

To manufacture an outer jacket of an aluminium phosphate-bonded cement, aluminium oxides of various particle sizes maybe mixed and worked into dilute phosphoric acid, optionally with the addition of burning-out agents and lubricants. The ceramic catalyst support is covered with this paste to a thickness of from 0.5 to 5 mm, preferably from 1 to 2 mm, and exposed to a heat treatment, in the course of which the outer jacket dries and sets.

To produce requisite flaws which have already been mentioned, such as micro-cracks or pores, the solids of the cement starting mixture can advantageously consist of 30 to 70% by weight of a coarse fraction of less than 28 mesh. A particle size of less than 28 mesh means that all particles have a smaller diameter than 590 μm.

According to another advantageous procedure, the solids of the cement starting mixture contain up to 20% by weight of substances which can be burnt out. Suitable substances which can be burnt out are inorganic or organic fillers such as, for ex-

ample,  $\text{NH}_4\text{HCO}_3$ , sawdust, cellulose fibres or plastics in a spherical or powdery form. Waxes from the group of the amide waxes, for example Wax C have proved particularly suitable. Amide waxes are condensation products of ethylene diamine and fatty acids. Wax C, of Farbwerke Hoechst AG., is derived from ethylenediamine and stearic acid, i.e., it consists of bis-

stearyl ethylene diamine. Finally, it can be expedient for the entire starting mixture to contain 1 to 10 % by weight of hydrocarbons substituted by hydroxyl groups as lubricants. Possible lubricants are here, for example, glycerol, polyglycols or higher alcohols.

The invention is illustrated by the following Examples.

#### Example 1

A fleece of 0.2 mm thickness manufactured in accordance with the customary papermaking technique from a composition consisting of 50% by weight of kaolin fibres and 50% by weight of cellulose fibres is corrugated in a device known from the corrugated board industry and brought together with a second, non-corrugated fleece layer to give a single-layer corrugated board which is glued with waterglass. Thereafter, this laminated structure is spirally wound up to an extent sufficient to give after sintering the appropriate diameter. A slip of the following composition is thereafter poured over this wound structure:

100g of 85% strength  $\text{Al}_2\text{O}_3$  slip  
60 g of water  
40 g of 10% strength polyvinylacetate dispersion.

The wound structure covered with slip in this way is dried in air at 30°C and subsequently sintered at 1,600°C and kept at this temperature for one hour.

#### Example 2

A fleece of 0.2 mm thickness manufactured in accordance with the customary papermaking technique from a composition consisting of 80% by weight of kaolin fibres and 20% by weight of cellulose fibres is corrugated in a device known from the corrugated board industry and brought together with a second, non-corrugated fleece layer to give a single-layer corrugated board which is glued with waterglass. Thereafter, this laminated structure is spirally wound as described in Example 1. The impregnation with slip is carried out in 2 stages, namely firstly by pouring as described in Example 1. Thereafter, the wound structure which has been sintered in a first calcination is impregnated for the second time by immersion in a slip which has the same com-

position as in the first impregnation. Thereafter, the second sintering is carried out at a substantially lower temperature, namely at 1,400°C, so that a substantially higher specific surface area results.

#### Example 3

This Example corresponds to Example 2 with a two-stage application of slip, and with the further characteristic that the second slip is itself already catalytically active. The inorganic material of the second slip consists of a mixture of 50% by weight of chromium oxide and 50% by weight of aluminium oxide.

#### Example 4

This Example corresponds to Example 1, with the wound structure being dipped into a slip of the following composition:

62% by weight of  $\text{Al}_2\text{O}_3$  powder.  
1% by weight of Mowiol (Trade Mark) polyvinyl alcohol  
37% by weight of water.

The wound structure impregnated in this way is allowed to drain. Thereafter warm air is blown through in order to dry it.

#### Example 5

To manufacture the outer jacket for the catalyst support, four different fractions of  $\alpha$ -aluminium oxide are mixed and subsequently incorporated, together with a Wax C, into dilute phosphoric acid so as to produce a cement mixture composed of 82% by weight of  $\alpha$ -aluminium oxide, 3% by weight of Wax C and 15% by weight of dilute phosphoric acid, and  $\alpha$ -aluminium oxide being composed of the following fractions:

28 mesh	48%
48 mesh	18%
90 mesh	26%
200 mesh	8%

100%

All particles of the specified fraction will pass through a sieve of the corresponding mesh size.

The essential feature in this composition is the combination of a coarse  $\alpha$ -aluminium oxide fraction of less than 28 mesh and of the burning-out material, Wax C.

The pasty mixture thus obtained has a viscosity of 4,000 cp  $\pm$  300 cp and is applied by means of an automatic spreading device onto the sintered catalyst support according to Examples 1 to 4.

To harden the outer jacket, the coated catalyst support is introduced into an electrically heated furnace. It is first dried by slow heating, in the course of which the outer jacket undergoes a preliminary con-

solidation. At about 200°C, the actual setting of the cement occurs. The heat treatment process is continued up to 400°C.

The catalyst support jacketed in this way has a compressive strength in the radial direction of over 100 kg/cm<sup>2</sup>, a high resistance to heat shock and a heat resistance at the temperatures which arise in motor vehicle exhaust gases.

The invention and advantageous details of the invention are explained in more detail, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 shows a greatly simplified representation of an enlarged section of a support structure manufactured according to the process of the invention. The support structure 6 consists of a corrugated layer 5 and a flat layer 4 which are alternately superposed and are combined to give a corrugated board structure. The half wave-height  $h/2$  and the half wave-length  $1/2$  referred to earlier in this specification are shown. The layers 4, 5 consist of refractory inorganic material 1 produced by sintering together refractory inorganic fibres with slip. If inorganic fibres containing silicate, such as, for example, kaolin, are used conjointly, regions which are enriched in SiO<sub>2</sub> are produced within the layers 4, 5. Channel-shaped pores 3 are distinctly recognisable in the areas in which the organic fibres of the fleece were present.

Figure 2 shows the catalyst support in a form rolled up to into a spiral. This form is suitable for use as an insert into tubular holders. Such catalyst cartridges are fitted into the exhaust gas system in order to save as much space as possible.

Figure 3 shows the catalyst support as a structure of square cross-section. This form is suitable for end uses where larger catalyst supports are involved.

Figure 4 shows a catalyst support 6 as in Figure 2 which is surrounded with a mechanically strong, refractory outer jacket 7 of shrinkage-free cement, with the actual catalyst support 6 consisting of the profiled layer 5 and the flat layer 4.

#### WHAT WE CLAIM IS:—

1. A process for the manufacture of a catalyst support consisting of layers of refractory inorganic material, at least every alternate layer being corrugated, wherein a fleece blank consisting of layers of fibrous fleece material comprising refractory inorganic fibres, at least every alternate layer being corrugated, is covered with a slip of refractory inorganic material, dried and sintered at a temperature within the range of from 1200 to 1800°C, the refractory inorganic material of the slip and the refractory inorganic fibres of the fleece

blank being so selected that on sintering the slip material and the fibrous material are sintered together.

2. A process as claimed in claim 1, wherein the fibrous fleece material consists of a mixture of refractory inorganic fibres and organic fibres.

3. A process as claimed in claim 2, wherein the fibrous fleece material consists of from 20 to 90% by weight of refractory inorganic fibres, the balance being organic fibres.

4. A process as claimed in claim 3, wherein the organic fibres comprise cellulose fibres.

5. A process as claimed in claim 4, wherein the organic fibres comprise cellulose fibres in such a quantity that they represent at least 5% by weight of the fibrous fleece material.

6. A process as claimed in any one of claim 1 to 5, wherein the refractory inorganic fibres of the fleece material contain aluminium oxide.

7. A process as claimed in claim 6, wherein the refractory inorganic fibres of the fleece material comprise mullite, sillimanite or kaolin.

8. A process as claimed in any one of claims 1 to 7, wherein the each layer of fibrous fleece material has a thickness within the range of from 0.1 to 0.5 mm and a weight per unit area of within the range of from 25 to 60 g/m<sup>2</sup>.

9. A process as claimed in claim 8, wherein each layer has a thickness within the range of from 0.15 to 0.3 mm.

10. A process as claimed in any one of claims 1 to 9, wherein after sintering the catalyst support is again covered with slip and is sintered at a temperature within the range of 1200 to 1400°C.

11. A process as claimed in any one of claims 1 to 10, wherein the refractory inorganic material of the slip comprises an oxide, a nitride, a carbide, a boride or a silicide.

12. A process as claimed in claim 10 wherein the refractory inorganic material of the slip contains aluminium oxide.

13. A process as claimed in claim 10 wherein the slip comprises an aqueous suspension of aluminium oxide powder.

14. A process as claimed in any one of claims 1 to 13, wherein the slip has a solids content of from 20 to 90% by weight.

15. A process as claimed in claim 14, wherein the slip has a solids content of from 40 to 70% by weight.

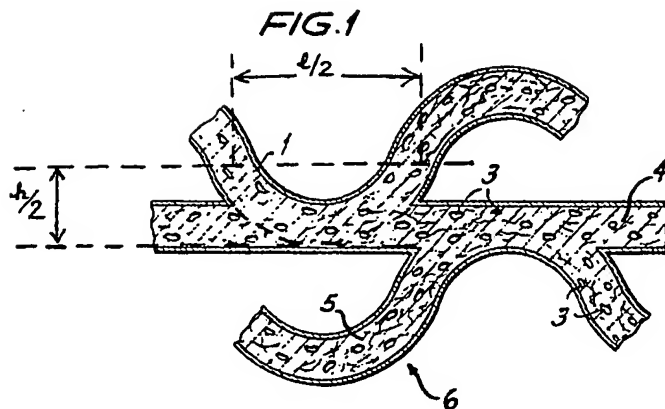
16. A process as claimed in any one of claims 1 to 15, wherein the slip additionally contains a substance capable of acting as a catalyst for the detoxication of exhaust gases.



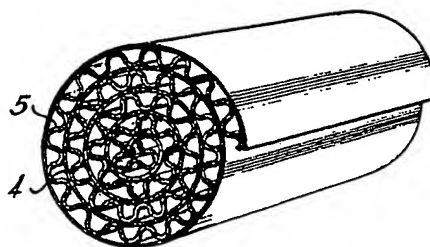
17. A process as claimed in any one of claims 1 to 16, wherein the refractory inorganic material of the slip is itself capable of acting as a catalyst for the detoxication of exhaust gases.
18. A process as claimed in any one of claims 1 to 7, wherein the fleece blank comprises alternate corrugated and substantially flat fleece layers.
19. A process for the manufacture of a catalyst support consisting of layers of refractory inorganic material, at least every alternate layer being corrugated, wherein a first support fleece of fibrous fleece material as specified in any one of claims 1 to 9 is corrugated, applied to a second support fleece of fibrous fleece material as specified in any one of claims 1 to 9, the resulting assembly is shaped, or a plurality of such assemblies are arranged and/or shaped, to form a fleece blank having a desired structure, in which at least every alternate layer is corrugated, and the fleece blank is treated as specified in any one of claims 1 and 10 to 17.
20. A process as claimed in claim 19, wherein the first support fleece is corrugated on a device for corrugating paper or cardboard.
21. A process as claimed in claim 19 or claim 20, wherein the second support fleece is substantially flat, and the assembly of the two fleeces is so shaped that the resulting fleece blank consists of alternating corrugated and substantially flat layers.
22. A process as claimed in any one of claims 19 to 21, wherein the assembly of the two fleeces is shaped by winding or stacking.
23. A process for the manufacture of a catalyst support consisting of layers of refractory material, at least every alternate layer being corrugated, which process is carried out substantially as described in any one of Examples 1 to 4 herein.
24. A catalyst support consisting of layers of refractory inorganic material, at least every alternate layer being corrugated, manufactured by a process as claimed in any one of claims 1 to 23.
25. A catalyst support as claimed in claim 24, which contains internal pores in positions in which organic fibres were present in the fleece blank.
26. A catalyst support as claimed in claim 24 or claim 25 consisting of alternating corrugated and flat layers, wherein the thickness at each bond between two adjacent layers is not substantially greater than the thickness of each layer.
27. A catalyst support as claimed in any one of claims 24 to 26, wherein the catalyst support is surrounded by a mechanically firm, refractory outer jacket of shrinkage-free ceramic cement (as hereinbefore defined).
28. A catalyst support as claimed in claim 27, wherein the outer jacket is of an aluminium phosphate-bonded ceramic cement.
29. A catalyst support substantially as hereinbefore described with reference to, and as shown in, any one of Figures 1 to 4 of the accompanying drawings.
30. A catalyst support substantially as described in any one of the Examples herein.
31. A process for the manufacture of a covered catalyst support as claimed in claim 27 or claim 28, wherein the catalyst support is covered with a slurry of shrinkage-free ceramic cement and the cement is allowed to dry and set at a temperature within the range of from 200 to 1000°C.
32. A process as claimed in claim 31, wherein the setting temperature is within the range of from 200 to 500°C.
33. A process as claimed in claim 32, wherein 30 to 70% by weight of the solids of the cement slurry consist of a coarse fraction of less than 28 mesh.
34. A process as claimed in claim 32 or claim 33, wherein the solids of the cement slurry contain up to 20% by weight of substances which are burnt out during setting.
35. A process as claimed in any one of claims 32 to 34, wherein the cement slurry contains 1 to 10% by weight, based on the total slurry, of hydrocarbons substituted by hydroxyl groups.
36. A catalyst for the detoxication of exhaust gases which comprises a substance capable of catalysing the detoxication of exhaust gases disposed on or forming part of a catalyst support as claimed in any one of claims 24 to 30.

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**FIG.2**



**FIG.3**

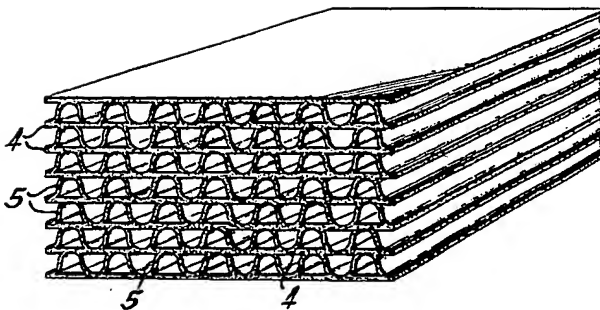


FIG. 4

